SYNTHESIS AND CHARACTERIZATION OF EARTH-ABUNDANT BASE METALS LAYER DOUBLE HYDROXIDES AND THEIR ENVIRONMENTAL APPLICABILITY

SYNOPSIS

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Introduction

Catalytic technologies play a vital role in the chemical industry, and provide an alternative pathway by lowering the activation energy barrier. There are two types of catalysis: heterogeneous and homogeneous (Mitchell et al., 2021). Because the catalytic active sites of homogenous catalysts are uniform, they exhibit good selectivity and efficiency in water splitting, pollutant degradation application (Cheng et al., 2022). Simultaneously, heterogeneous catalysts are key to a sustainable future because heterogeneous catalysis is at the center of the chemical and energy industries that demonstrated dynamic properties in a variety of sectors, including medicinal compounds, polymers, fine and heavy chemicals production. The following processes are involved in these catalysts: chemisorption of the reactant on the catalyst surface, desorption of the reaction products from the surface, and chemical reaction on the catalyst surface (Chen et al., 2023). Catalysis is helpful for green chemical processes and reduce environmental effects. Enhancing selectivity is essential to creating catalysts connected to green chemistry (Becker, Manske & Randl, 2022; Chen et al., 2021). The application of metals such as catalysts and anionic exchangers in supercapacitors, electrolytes, and photoactive materials (Jing, Dong & Zhang, 2020) is greatly influenced by their shape, size, and morphology. Green chemistry focus on designing products for the next generation because the “design of chemical products and processes reduces the use and generation of hazardous substances” (Locatelli et al., 2023). Catalysts can also be derived from layered double hydroxide (LDH) materials, and intercalated clay exhibits excellent catalytic activity at relatively lower temperatures. LDH materials belong to the clay family. Clay is a natural, earthy, fine-grained material composed of crystalline minerals and intercalated by certain groups of hydrous aluminium, magnesium, and iron silicates that may contain sodium, calcium, potassium, and other ions (Padmalosan et al., 2023). Clays are classified into two classes: anionic clays and cationic clays. Brucite and anionic clays are defined by their chemical composition, basal spacing, and stacking sequence. Anionic clays are usually synthesized by precipitation methods and used in ion exchangers and scavengers in industry and laboratories, producing reactive and stereoselective processes (El-habacha et al., 2023).

Anionic clays combine of natural and synthetic layers of mixed hydroxide containing exchangeable anions. The anionic clay based on hydrotalcite compounds has found many practical applications. These include a high surface area, basic properties, the formation

of homogeneous oxide mixtures with very small crystal size that are stable to thermal treatment, which is formed by reduction from small and thermally stable metal crystallization, and memory effects that allow the original hydrotalcite structure to be rebuilt under mild conditions using water solutions containing different anions as the product of the thermal treatment (Sharma et al., 2023; Kumari et al., 2023). Smectic/Cationic (or swelling clays) are common constituents of such rocks and are often present in faults sealing potential storage reservoirs, at least at depths up to about ∼2–3 or 3.5 km under temperatures of 100°C. Smectites generally start to transform into the non-swelling clay mineral illite (Taher et al., 2023). Cationic clays are mainly obtained from natural materials such as calcite and quartz. The crystal structure of smectites is characterized by octahedral silicate sheets (O) sandwiched between tetrahedral sheets (T) to form TOT layers separated by cation-bearing interlayers (Amaly et al., 2022).

LDH represented by a class of 2D layered materials belonging to the hydrotalcite group like compound or anionic clays. Hydrotalcite-like compounds refer to anionic clays with cationic clays and an important class of ionic lamellar solids. The general formula of LDHs: $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2(A^{n-})_{x/n}]\cdot yH_2O$ where M^{2+} and M^{3+} the divalent (Mg^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and trivalent metal cations (Al^{3+}, Fe^{3+}, Co^{3+}, Cr^{3+}, Mn^{3+} ,In^{3+}),A^{n-} are inorganic and organic anions such as CO_3^{2-}, OH^-, Cl^-, NO_3^-, n is the number of interlayer water, $x = M^{3+}/(M^{2+}+ M^{3+})$ layer charge density or molar ratio (Bernard et al., 2022). LDHs are known as hydrotalcite compound with a brucite-like structure and hydrotalcite found in natural minerals. The H atom toward the interlayer depends on the complex layered structure in the mineral brucite $(OH)_2$, where magnesium ions are found in octahedral sites with six OH^- groups at the vertices. This mineral is used for drug delivery in pharmaceuticals, organic waste adsorption, and catalysis (Kumari et al., 2022). When LDHs undergo thermal treatment, their layer structure breaks down and is changed to mixed metal oxide, which results in LDHs with a large specific surface area (Soni et al., 2023).

Layered double hydroxide (LDH) is the most important class of solid catalysts. LDHs had favorable features, like a large surface area, strong thermal stability, and high regeneration efficiencies, for the adsorption of pollutants. Current studies have demonstrated the remarkable adaptability of LDH-like materials in customizing their chemical and physical characteristics for usage in many applications related to photocatalysis and electrocatalysis (Rohit et al., 2021). The layered double hydroxide

can be prepared using sol-gel, hydrothermal, and co-precipitation methods (George & Saravana Kumar, 2020). LDH materials is used as the visible-light photocatalyst for use in photovoltaic catalytic water splitting applications as well as anode material for lithium-ion batteries. LDH is a useful substance that is utilized in solar applications as an electrode material (Boumeriame et al., 2022; Pallikkara & Ramakrishna, 2021).

Literature review

Layered double hydroxides belong to the class of two-dimensional anionic clay material and have been explored as catalytic materials in various photo-, electro- and photoelectron - related applications. The recent published research reports investigated their role and applicability in environment related applications summarized as and directed further to sightsaw their potentialities in field of environment and energy fields.

Pesic et al. (1992) prepared the synthetic hydrotalcite-like material by the hydrothermal method and structural characterization during the decomposition of water and carbon dioxide, which evolved and changed the crystal structure of the materials due to the chemical analysis of hydrotalcite materials.

Costantino et al. (1998) prepared the hydrogen site-like compound by the co-precipitation method, resulting in the formation of the hydrotalcite with Cl^- and OH^- as the balancing anions due to being washed with water and hydrated inside the material at 150°C. The carbonate is then converted into the chloride form.

Khan & O'Hare (2002) studied the layer of double hydroxide material for the anion exchange intercalation reactions. Naturally occurring LDH can be found in two polymorphic forms: rhombohedral and hexagonal.

Lee et al. (2010) studied anthraquinone sulfonate (AQS) sensitized cell initial conversion values of 160% to improve cell performance because of the variable compositions of LDH.

Liu et al. (2013) ZnTi mixed metal oxide synthesized by the urea method and used it as electrodes for the dye-sensitized solar cells by using the N719 synthetic dye and showed good power conversion efficiency

Ho et al. (2014) studied layer double hydroxide-based polymer gel electrolytes, which are traditional liquid electrolytes for DSSC application, and polymer electrolytes better than 92% liquid electrolytes and it shows that the open circuit voltage is 0.74V and gelled electrolyte-based DSSC is 0.79V.

Zhang et al. (2014) studied ZnAl layer double hydroxide synthesized by the urea decomposition method and showed the 0.015% best photo conversion efficiency in photovoltaic applications.

Bella et al. (2016) studied floating flexible transparent DSSC of TiO_2 nanotubes-based and it was reported that 5% power conversion efficiency exceeding under sun irradiation.

Parida et al. (2012) synthesized different anions (chloride, nitrate, and carbonate) intercalated with Zn/Fe LDH that showed the effective photocatalytic degradation of azo dyes.

Huang et al. (2015) studied the photo-catalytic activity of AgCl-BiOCl-NiFe LDH composites for the decolorization of RhB under visible light irradiation, it showed that 97.8% dye was degraded in 60 min.

Cao et al. (2016) studied zinc-titanium mixed metal oxide on the LDH precursors, and graphene/ZnTi mixed metal oxide materials were used in the photoanode of the CdS Quantum Dot Sensitized Solar Cells (QDSSCs).

Zhang et al. (2017) studied the dye-sensitized solar cell by a facile calcination method and by using the Rutheizer 535-bisTBA (N719) dye it showed the 0.0129% power conversion efficiency of photovoltaic behaviors of solar cells.

Feng et al. (2017) studied CoFe-layered double hydroxide, which exhibits the best electrocatalytic performance in the oxygen evolution reaction, and a $100mA/cm^{-2}$ current density was shown in the 3D electrode.

Liu et al. (2018) studied the ZnSn layer double hydroxide and its application in the DSSC as a photoanode and explored the new efficient photoanode based on mixed metal oxide which showed that the 1.288% best efficiency.

Foruzin & Rezvani (2019) NiCoFe-layer double hydroxide synthesized by coprecipitation and ultrasonication methods. This is a suitable electrocatalyst because it shows the good stability for water oxidation reactions in the presence of 0.1 M KOH.

Zhou et al. (2019) carried out 3D novel flower sheet nanostructures and materials fabricated for batteries and supercapacitors, such as carbon material. The study showed highest specific capacitance ($1187.2Fg^{-1}$ at $1Ag^{-1}$) and good stability (97% retention after 1000 cycles).

Li, Zhang & Liu (2020) prepared 3D NiFe-layered double hydroxide-polyoxometalate synthesized by the one-step hydrothermal method, a highly efficient bifunctional catalyst for overall water splitting. The water-splitting current density was $10mA/cm^2$ and operates for 20 hours.

Ganiyu et al. (2020) studied CoFe-layer double hydroxide synthesized by solvothermal method and it exhibits sensitized good reusability of 60%.

Aslam et al. (2020) reported that DSSC technology generated about 49.6% of US dollars in the photovoltaic market in 2014, and that increased the 12% from 2015 to 2022.

Kumar et al. (2020) reported in this review that different photovoltaic technologies, such as ruthenium-based polymers, increase the electrolyte, which is an important feature for the commercialization of DSSC.

Pallikkara & Ramakrishnan (2020) reported that after this review of the modification of the photoanode, the maximum photoconversion efficiency of DSSC remained at 13%, indicating a further improved approach in the future to the improvement of the convention of DSSC.

Ge et al. (2021) prepared Cu-doped ZnO nanoparticles by hydrothermal methods and solar cells with ZnO 0.25 wt% it showed that photoanode achieves the highest short circuit current density is 7.12 mA/cm^2, and 1.5 % the photoconversion efficiency.

Tian et al. (2019) synthesized NiFe layer double hydroxide synthesized by the hydrothermal method. Its use as anode materials in lithium-ion batteries showed superior lithium storage capacity with 1202 mAh/g^{-1} even at 2000 mA/g^{-1}.

Almutairi, Farooq & AlSalhi (2022) studied dye solar cells using the natural dye beetroot and it showed the short-circuit density of 130$\mu A/cm^2$ and an open-circuit voltage of 0.38V with showed a 1.5-intensity linear behaviour at high intensity.

Yong et al. (2022) studied that the CoCuFe, ZnNiFe, ZnCoFe, ZnCuFe, CoGaFe layer double hydroxide, and CoGaFe - LDH are the best electrocatalysts, with an overpotential value of 369.9 mV in 10mA/cm^2 and it shows that the tafel slope of 64.8 mV/dec.

Research gap identification

Many researchers have studied the synthesis and physiochemical properties of hydrotalcite materials but there is less literature reported on the hydrotalcite materials as a catalyst. So, our main focus will be on synthesizing and studying the catalytic properties of hydrotalcite type anionic clays in the degradation of organic or inorganic pollutants from various industries.

Objectives

- Synthesis and screening of various layer double hydroxide materials composed of Ni, Co, Al, Fe, Zn.

- To characterize the layer double hydroxide material using different characterization techniques like XRD, FTIR, SEM-EDX, and TEM.
- To evaluate the layer double hydroxide material for environmental applicability and select the best layer double hydroxide for the desired application.

Proposed methodology

❖ Chemical required

For the synthesis of various layer double hydroxide material chemical such as will be iron nitrate, zinc nitrate, copper nitrate, sodium hydroxide pellet, sodium carbonate, etc. will be explored.

❖ Apparatus required

Apparatus like magnetic stirrer, beaker, thermometer, pH meter measuring cylinder, three neck round bottom flask, reflux condenser, filter paper, funnel, oven, etc. will be required for hydrotalcite materials synthesis.

❖ Method

The preparations of layer double hydroxide material will be performed by mixing a fixed amount of divalent and trivalent metal salts with solution of NaOH and Na_2CO_3 under a fixed pH value. Obtained slurry will be maintained for 24 hours for post-treatment under the stirring with heating. The precipitated crystallized particles will be cooled, filter, washed with deionized water and dried at 110℃ for 24 hours. The structural characteristics of synthesized samples will be analyzed by various techniques (XRD, FTIR, SEM-EDX, and TEM). The environmental applicability of these synthesized clay materials will be evaluated in terms of their photo- and photoelectric-catalytic efficiency in dye-sensitized solar cell and dye degradation advanced oxidation processes.

Thesis outline

Chapter 1 (Introduction) This chapter will include the detailed introduction of layer double hydroxide base catalytic materials.

Chapter 2 (Literature review) This chapter will include the deep literature survey of layer double hydroxide, mixed metal oxide, and application activities. This chapter also includes the research gap identification.

Chapter 3 (Experimental and Characterization technique) This chapters will give a detailed description of chemical operators used for the synthesis of layer double hydroxide and also includes the details of various techniques.

Chapter 4 (Results and Discussion) This chapter will deals with the results obtained in this research. It also includes the discussion and comparison of results with previously published reports.

Chapter 5 (Conclusion) This chapter will include a summary of the entire study according to the objective along with the conclusion, and future scope of the research.

Chapter 6 (References) This chapter will enlist the references of books reports, research papers, project reports, and patents followed in this study.

References

Amaly, N., Pandey, P., El-Moghazy, A. Y., Sun, G. & Pandey, P. K., (2022) Cationic microcrystalline cellulose-Montmorillonite composite aerogel for preconcentration of inorganic anions from dairy wastewater. *Talanta*. 242, 123281. Available from: https://doi.org/10.1016/j.talanta.2022.123281

Almutairi, M. A., Farooq, W. A. & AlSalhi, M. S., (2022) Photovoltaic and impedance properties of dye-sensitized solar cell based on nature dye from beetroot. *Current Applied Physics.* 40, 119-125. Available from: https://doi.org/10.1016/j.cap.2021.07.010

Aslam, A., Mehmood, U., Arshad, M. H., Ishfaq, A., Zaheer, J., Khan, A. U. H. & Sufyan, M., (2020) Dye-sensitized solar cells (DSSCs) as a potential photovoltaic technology for the self-powered internet of things (IoTs) applications. *Solar Energy*. 207, 874-892. Available from: https://doi.org/10.1016/j.solener.2020.07.029

Bernard, E., Zucha, W. J., Lothenbach, B. & Mäder, U., (2022) Stability of hydrotalcite (Mg-Al layered double hydroxide) in presence of different anions. *Cement and Concrete Research*. 152, 106674. Available from: https://doi.org/10.1016/j.cemconres.2021.106674

Boumeriame, H., Da Silva, E. S., Cherevan, A. S., Chafik, T., Faria, J. L. & Eder, D., (2022) Layered double hydroxide (LDH)-based materials: A mini-review on strategies to improve the performance for photocatalytic water splitting. *Journal of Energy Chemistry*. 64, 406-431. Available from: https://doi.org/10.1016/j.jechem.2021.04.050

Becker, J., Manske, C. & Randl, S., (2022) Green chemistry and sustainability metrics in the pharmaceutical manufacturing sector. *Current Opinion in Green and Sustainable Chemistry*. *33*, 100562. Available from:

https://doi.org/10.1016/j.cogsc.2021.100562

Bella, F., Lamberti, A., Bianco, S., Tresso, E., Gerbaldi, C. & Pirri, C. F., (2016) Floating, flexible polymeric dye-sensitized solar-cell architecture: the way of near-future photovoltaics. *Advanced Materials Technologies*. 1 (2). Available from: https://doi.org/10.1002/admt.201600002

Chen, J., Zhang, Y., Zhang, Z., Hou, D., Bai, F., Han, Y., Zhang, C., Zhang, Y. & Hu, J., (2023) Metal-support interactions for heterogeneous catalysis: mechanisms, characterization techniques and applications. *Journal of Materials Chemistry.* Available from: https://doi.org/10.1039/D2TA10036C

Cheng, X., Lei, A., Mei, T. S., Xu, H. C., Xu, K. & Zeng, C., (2022) Recent applications of homogeneous catalysis in electrochemical organic synthesis. *CCS Chemistry*. 4 (4), 1120-1152. Available from: https://doi.org/10.31635/ccschem.021.202101451

Cao, J., Zhu, Y., Yang, X., Chen, Y., Li, Y., Xiao, H., Hou, W. & Liu, J., (2016) The promising photo anode of graphene/zinc titanium mixed metal oxides for the CdS quantum dot-sensitized solar cell. *Solar Energy Materials and Solar Cells*. 157, 814-819. Available from: https://doi.org/10.1016/j.solmat.2016.08.003

Chen, S., Chang, X., Sun, G., Zhang, T., Xu, Y., Wang, Y., Pei, C. & Gong, J., (2021) Propane dehydrogenation: catalyst development, new chemistry, and emerging technologies. *Chemical Society Reviews.* 50 (5), 3315-3354. Available from: https://doi.org/10.1351/pac200173010103

Costantino, U., Marmottini, F., Nocchetti, M. & Vivani, R., (1998) New synthetic routes to hydrotalcite-like compounds-characterization and properties of the obtained materials. *European Journal of Inorganic.* Available from: https://doi.org/10.1002/(SICI)1099-0682(199810)1998:10%3C1439::AID-EJIC1439%3E3.0.CO;2-1

El-habacha, M., Miyah, Y., Lagdali, S., Mahmoudy, G., Dabagh, A., Chiban, M., Sinan, F., Iaich, S. & Zerbet, M., (2023) General overview to understand the adsorption mechanism of textile dyes and heavy metals on the surface of different clay materials. *Arabian Journal of Chemistry*. 16 (11), 105248. Available from: https://doi.org/10.1016/j.arabjc.2023.105248

Foruzin, L. J., Rezvani, Z. & Nejati, K., (2019) TiO_2@NiAl-Layered double oxide nanocomposite: An excellent photoanode for a dye sensitized solar cell. *Solar*

Energy. 186, 106-112. Available from: https://doi.org/10.1016/j.solener.2019.05.005

Feng, L., Li, A., Li, Y., Liu, J., Wang, L., Huang, L., Wang, Y. & Ge, X., (2017) A highly active CoFe layered double hydroxide for water splitting. *Chem Plus Chem*. 82 (3), 483-488. Available from: https://doi.org/10.1002/cplu.201700005

Ge, Z., Wang, C., Chen, T., Chen, Z., Wang, T., Guo, L., Qi, G. & Liu, J., (2021) Preparation of Cu-doped ZnO nanoparticles via layered double hydroxide and application for dye-sensitized solar cells. *Journal of Physics and Chemistry of Solids*. 150, 109833. Available from: https://doi.org/10.1016/j.jpcs.2020.109833

George, G. & Saravanakumar, M. P., (2020) Fabrication and performance analysis of a low cost, Pt free counter electrode using carbon coated ZnAl layered double hydroxide (C/ZnAl-LDH) for dye sensitized solar cells. *Solar Energy*. 202, 144-154. Available from: https://doi.org/10.1016/j.solener.2020.03.113

Ganiyu, S. O., Le, T. X. H., Bechelany, M., Esposito, G., van Hullebusch, E. D., Oturan, M. A. & Cretin, M., 2017. A hierarchical CoFe-layered double hydroxide modified carbon-felt cathode for heterogeneous electro-Fenton process. *Journal of Materials Chemistry A*. 5 (7), 3655-3666. Available from: https://doi.org/10.1039/C6TA09100H

Huang, D., Ma, J., Yu, L., Wu, D., Wang, K., Yang, M., Papoulis, D. & Komarneni, S., (2015) AgCl and BiOCl composited with NiFe-LDH for enhanced photo-degradation of Rhodamine B. *Separation and Purification Technology*. 156, 789-794. Available from: https://doi.org/10.1016/j.seppur.2015.11.003

Hsu-Wen, H., Wei-Yun, C., Yu-Chun, L., Tzu-Chien, W. & Shih-Yuan, L., (2014) Layered Double Hydroxides as an Effective Additive in Polymer Gelled Electrolyte based Dye-Sensitized Solar Cells. Available from: https://doi.org/10.1021/am504912d

Ho, H. W., Cheng, W. Y., Lo, Y. C., Wei, T. C. & Lu, S. Y., (2014) Layered double hydroxides as an effective additive in polymer gelled electrolyte-based dye-sensitized solar cells. *ACS Applied Materials and Interfaces*. 6 (20) 17518-17525. Available from: https://doi.org/10.1021/am504912d

Jing, C., Dong, B. & Zhang, Y., (2020) Chemical modifications of layered double hydroxides in the supercapacitor. *Energy and Environmental Materials*. 3 (3), 346-379. Available from: https://doi.org/10.1002/eem2.12116

Kumari, S., Sharma, V., Sharma, A., Sharma, A., Singh, B. J. & Sharma, A. K., (2023) Layered double hydroxides: a gleam on their synthetic routes with biomedical applications. *International Journal on Interactive Design and Manufacturing (IJIDeM)*. 1-9. Available from: *https://link.springer.com/article/10.1007/s12008-023-01333-5*

Kumari, S., Thakur, N., Kumar, R., Thakur, R. C. & Sharma, A., (2022) Effect of synthetic parameters on crystallinity of hydrotalcite-like anionic clays with elucidation and identification through X-ray Diffraction analysis. *ECS Transactions*. 107 (1), 18903. Available from: 10.1149/10701.18903ecst

Kumar, D. K., Kříž, J., Bennett, N., Chen, B., Upadhayaya, H., Reddy, K. R. & Sadhu, V., (2020) Functionalized metal oxide nanoparticles for efficient dye-sensitized solar cells (DSSCs): A review. *Materials Science for Energy Technologies*. 3, 472-481. Available from: https://doi.org/10.1039/C1JM11594D

Khan, A. I. & O'Hare, D., (2002) Intercalation chemistry of layered double hydroxides: recent developments and applications. *Journal of Materials Chemistry*. 12 (11), 3191-3198. Available from: https://doi.org/10.1039/B204076J

Locatelli, M., Kabir, A., Perrucci, M., Ulusoy, S., Ulusoy, H. I. & Ali, I., (2023) Green profile tools: current status and future perspectives. *Advances in Sample Preparation*. 100068. Available from: https://doi.org/10.1016/j.sampre.2023.100068

Li, C., Zhang, Z. & Liu, R., (2020) In situ growth of 3D NiFe LDH-POM micro-flowers on nickel foam for overall water splitting. *Small*. 16 (46), 2003777. Available from: https://doi.org/10.1002/smll.202003777

Liu, S., Liu, D., Liu, J., Wang, D., Zhu, Y., Li, H., Du, N., Xiao, H., Hao, X. & Liu, J., (2018) The prospective photo anode composed of zinc tin mixed metal oxides for the dye-sensitized solar cells. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 547, 111-116. Available from: https://doi.org/10.1016/j.colsurfa.2018.03.051

Liu, J., Qin, Y., Zhang, L., Xiao, H., Song, J., Liu, D., Leng, M., Hou, W. & Du, N., (2013) Mixed metal oxides for dye-sensitized solar cell using zinc titanium layered double hydroxide as precursor. In *Micro/Nano Materials, Devices, and Systems*. 25-30. Available from: https://doi.org/10.1117/12.2033532

Lee, J. H., Chang, J., Cha, J. H., Jung, D. Y., Kim, S. S. & Kim, J. M., (2010) Anthraquinone Sulfonate Modified, Layered Double Hydroxide Nanosheets for

Dye-Sensitized Solar Cells. *Chemistry A Europea Journal*.16 (28), 82968299. Available from: https://doi.org/10.1002/chem.201000703

Mitchell, S., Qin, R., Zheng, N. & Pérez-Ramírez, J., (2021) Nanoscale engineering of catalytic materials for sustainable technologies. *Nature Nanotechnology*. 16 (2), 129-139. Available from: https://doi.org/10.1038/s41565-020-00799-8

Padmalosan, P., Vanitha, S., Kumar, V. S., Anish, M., Tiwari, R., Dhapekar, N. K. & Yadav, A. S., (2023) An investigation on the use of waste materials from industrial processes in clay brick production. *Materials Today: Proceedings*. Available from: https://doi.org/10.1016/j.matpr.2023.01.238

Pallikkara, A. & Ramakrishnan, K., (2021) Efficient charge collection of photoanodes and light absorption of photosensitizers: A review. *International Journal of Energy Research*. 45 (2), 1425-1448. Available from: https://doi.org/10.1002/er.5941

Parida, K. M. & Mohapatra, L., (2012) Carbonate intercalated Zn/Fe layered double hydroxide: a novel photocatalyst for the enhanced photo degradation of azo dyes. *Chemical Engineering Journal*. 179, 131-139. Available from: https://doi.org/10.1016/j.cej.2011.10.070

Pesic, L., Salipurovic, S., Markovic, V., Vucelic, D., Kagunya, W. & Jones, W., (1992) Thermal characteristics of a synthetic hydrotalcite-like material. *Journal of Materials Chemistry*. 2 (10), 1069-1073. Available from: https://doi.org/10.1039/JM9920201069

Rohit, R. C., Jagadale, A. D., Shinde, S. K. & Kim, D. Y., (2021) A review on electrodeposited layered double hydroxides for energy and environmental applications. *Materials Today Communications*. 27, 102275. Available from: https://doi.org/10.1016/j.mtcomm.2021.102275

Sharma, A., Kumari, S., Sharma, S., Singh, T., Kumar, S., Thakur, A., Bhatia, S. K. and Sharma, A. K., (2023) Layered Double Hydroxides: An insight into the role of Hydrotalcite-type Anionic Clays in Energy and Environmental applications with Current Progress and Recent Prospects. *Materials Today Sustainability*. 100399 Available from: https://doi.org/10.1016/j.mtsust.2023.100399

Soni S, Kumari S, Sharma A, Sharma AK (2023) MIIAl-CO_3 Based Layered Hydroxides: Synthesis and Photocatalytic Efficiency Against Anionic Dye. *Taylor Francis*. Available from: https://doi,org/10,4324/9781003388982-9

Taher, T., Munandar, A., Mawaddah, N., Wisnubroto, M. S., Siregar, P. M. S. B. N., Palapa, N. R., Lesbani, A. & Wibowo, Y. G., (2023) Synthesis and

characterization of montmorillonite-Mixed metal oxide composite and its adsorption performance for anionic and cationic dyes removal. *Inorganic Chemistry Communications*. 147, 110231. Available from: https://doi.org/10.1016/j.inoche.2022.110231

Tian, M., Liu, C., Neale, Z. G., Zheng, J., Long, D. & Cao, G., (2019) Chemically bonding NiFe-LDH nanosheets on rGO for superior lithium-ion capacitors. *ACS Applied Materials and Interfaces*. 11 (39), 35977-35986. Available from: https://doi.org/10.1039/D2RA01980A

Yong, J. D., Valdez, R., Armenta, M. Á., Arjona, N., Pina-Luis, G. & Olivas, A., (2022) Influence of Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, and Ga^{3+} on the iron-based trimetallic layered double hydroxides for water oxidation. *RSC Advances*. 12 (26), 1695516965. Available from: https://doi.org/10.1021/acsami.9b10719

Zhou, Y., Li, J., Yang, Y., Luo, B., Zhang, X., Fong, E., Chu, W. & Huang, K., (2019) Unique 3D flower-on-sheet nanostructure of NiCo LDHs: Controllable microwave-assisted synthesis and its application for advanced supercapacitors. *Journal of Alloys and Compounds*. 788, 1029-1036. Available from: https://doi.org/10.1016/j.jallcom.2019.02.328

Zhang, L., Yao, H., Li, Z., Sun, P., Liu, F., Dong, C., Wang, J., Li, Z., Wu, M., Zhang, C. & Zhao, B., (2017) Synthesis of delaminated layered double hydroxides and their assembly with graphene oxide for supercapacitor application. *Journal of Alloys and Compounds*. 711, 31-41. Available from; https://doi.org/10.1016/j.jallcom.2017.03.348

Zhang, L., Liu, J., Xiao, H., Liu, D., Qin, Y., Wu, H., Li, H., Du, N. & Hou, W., (2014) Preparation and properties of mixed metal oxides based layered double hydroxide as anode materials for dye-sensitized solar cell. *Chemical Engineering Journal*. 250, 1-5. Available from: https://doi.org/10.1016/j.cej.2014.03.098.

CERTIFICATE
(SYNOPSIS APPROVAL CERTIFICATE)

This is to certify that the synopsis for Ph.D. thesis titled, **"SYNTHESIS AND CHARACTERIZATION OF EARTH-ABUNDANT BASE METALS LAYER DOUBLE HYDROXIDES AND THEIR ENVIRONMENTAL APPLICABILITY"**, submitted by **Ms. ANJALI KUMARI** to the Career Point University, Hamirpur (H.P.), India in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY** in the Department of Chemistry, School of **Basic and Applied Sciences** has been approved by the Research Advisory Committee (RAC) after an Oral Examination of the student on dated 03.06.2024.

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